

Superconductivity in novel Ge-based skutterudites: $\{\text{Sr}, \text{Ba}\}\text{Pt}_4\text{Ge}_{12}$

E. Bauer¹, A. Grytsiv², Xing-Qiu Chen^{2,4}, N. Melnychenko-Koblyuk², G. Hilscher¹, H. Kaldarar¹, H. Michor¹, E. Royanian¹, G. Giester³, M. Rotter², R. Podloucky² & P. Rogl²

¹*Institute of Solid State Physics, Vienna University of Technology, A-1040 Wien, Austria*

²*Institute of Physical Chemistry, University of Vienna, A-1090 Wien, Austria*

³*Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, A-1090 Wien, Austria and*

⁴*School of Materials and Metallurgy, Northeastern University, Shenyang, 110004, P. R. China*

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Combining experiments and *ab initio* models we report on $\text{SrPt}_4\text{Ge}_{12}$ and $\text{BaPt}_4\text{Ge}_{12}$ as members of a novel class of superconducting skutterudites, where Sr or Ba atoms stabilize a framework entirely formed by Ge-atoms. Below $T_c = 5.35$ K, and 5.10 K for $\text{BaPt}_4\text{Ge}_{12}$ and $\text{SrPt}_4\text{Ge}_{12}$, respectively, electron-phonon coupled superconductivity emerges, ascribed to intrinsic features of the Pt-Ge framework, where Ge-*p* states dominate the electronic structure at the Fermi energy.

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Cage-forming compounds such as zeolites, fullerenes, clathrates or skutterudites have been proven not only of scientific but also of significant technological interest. The ability of these materials to accommodate guest filler species constitutes a wide range of varying chemical and physical properties, comprising magnetic order, heavy fermion behavior, Fermi - and non-Fermi liquid features, or conventional or unconventional superconductivity (SC). For recent reviews regarding the superconducting properties of these classes of materials see Ref. [1, 2, 3]. Most impressive, however, is the exceptional thermoelectric performance in some of the clathrates and skutterudites [4].

A structural-chemical description classifies skutterudites as cage compounds. The simple structure, however, acts as a prototype for a large class of compounds including binary as well as ternary and higher order representatives. Hitherto, cage forming elements of skutterudites are essentially based on volatile and/or toxic pnictogens ($X = \text{P}, \text{As}, \text{Sb}$). Building blocks in the framework are 8 tilted octahedra per unit cell enclosing two icosahedral cages. Each of the octahedra is centered by a transition metal atom like Co or its homologues (Rh, Ir).

Motivated by the known manifold of interesting physical properties among skutterudites, we searched for ternary and/or higher order compounds exploiting the combination of (i) a high density of *d*-states of a platinum group metal at the Fermi level with (ii) a rigid framework of rather covalently four-bonded atoms such as Si and/or Ge. Thereby a novel family of Ge based skutterudites, $\text{SrPt}_4\text{Ge}_{12}$ and $\text{BaPt}_4\text{Ge}_{12}$ has been identified. The aim of the present work is a study of the stability and the characterization of bulk properties by means of resistivity, magnetization, specific heat and band structure calculations. For both compounds, the low temperature behavior is dominated by the appearance of superconductivity around 5 K.

$\{\text{Sr}, \text{Ba}\}\text{Pt}_4\text{Ge}_{12}$ were prepared from stoichiometric amounts of high purity elements by argon arc melting and subsequently heat treated in evacuated quartz capsules at 800°C for two weeks. Phase purity and lattice

parameters were checked by EMPA and x-ray diffraction. Bulk properties of these novel skutterudites were obtained by a number of standard techniques, details are summarized in Ref [5]. Density functional theory (DFT) was applied using the Vienna *ab initio* simulation package (VASP) [6, 7] with a fully relativistic spin-orbit coupling approach [8, 9]. The Brillouin zone was sampled with $5 \times 5 \times 5$ Monkhorst-Pack \vec{k} -point grids. The exchange-correlation functional was treated within the local density approximation.

The crystal structure of $\{\text{Sr}, \text{Ba}\}\text{Pt}_4\text{Ge}_{12}$ was determined from Kappa-CCD single crystal X-ray data and found to be cubic, isotypic with the filled skutterudite type $\text{LaFe}_4\text{Sb}_{12}$ [10]. Structure and lattice parameters are collected in Table I. Occupation factors were refined, corresponding to a full occupancy of the Pt and Ge sublattices. Although not revealed from single crystal refinement, minor deviations (up to 3 %) from full occupancy are possible for the Ba and Sr atoms. Since the size of the Ge-framework is significantly smaller than the corresponding Sb-framework, effective bonding between the framework cages (two icosahedra per unit cell) and the Ba(Sr)-center atoms is ensured. As a consequence of this stronger bond between cage and guest atom, we observe very regular thermal atom displacement factors (ADP) on all atoms. The temperature dependencies of ADP's in the temperature region from 100 to 300 K reveal for all atoms similar trends: typical rattling modes caused by the heavy guest atoms in Sb-based skutterudites are absent in $\{\text{Ba}, \text{Sr}\}\text{Pt}_4\text{Ge}_{12}$. The structural parameters as derived from DFT calculations are in excellent agreement with the experimental data. In order to analyze the thermodynamical stability of $\text{XPt}_4\text{Ge}_{12}$ ($X=\text{Ba}, \text{Sr}$) compounds we also calculated the total energy for a hypothetical compound $\text{Pt}_4\text{Ge}_{12}$. The bonding energy E_X for guest atom X is obtained from the relation $E_X = U_{\text{XPt}_4\text{Ge}_{12}}^{\text{DFT}} - U_{\text{Pt}_4\text{Ge}_{12}}^{\text{DFT}} - U_X^{\text{DFT}}$ in which U^{DFT} denotes the corresponding total energy of the compound or elemental solid in its equilibrium state. The values $E_{\text{Ba}} = -3.24$ eV and $E_{\text{Sr}} = -3.38$ eV emphasize the stabilizing effect of the Ba and Sr guest atoms.

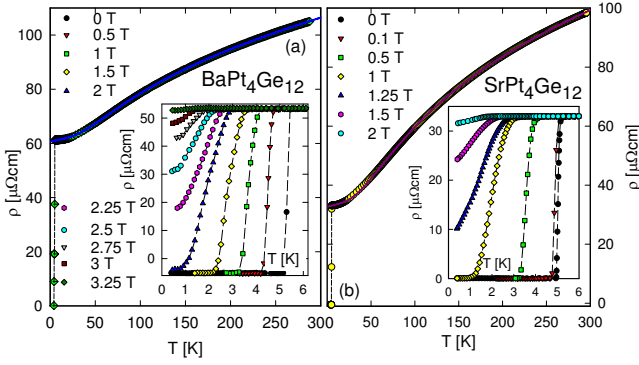


FIG. 1: (Color online) Temperature dependent electrical resistivity ρ of BaPt₄Ge₁₂ (a) and SrPt₄Ge₁₂ (b). Both insets show the field dependence of $\rho(T)$.

Superconductivity is found for BaPt₄Ge₁₂ and SrPt₄Ge₁₂ from resistivity measurements using polycrystalline samples at $T_c \approx 5.3$ K and 5.1 K, respectively (compare Fig. 1(a,b)). The normal state regions, $T > T_c$ of these ternary compounds do not behave like simple metals, since the standard model of the electrical resistivity of metallic systems, i.e., the Bloch-Grüneisen formula is not applicable. Such observations were made in many superconducting materials and may be attributed to a substantial electron-phonon interaction strength, responsible for the formation of Cooper pairs in conventional superconductors. Rather, the overall $\rho(T)$ -dependence of both skutterudites follows the model of Woodward and Cody [11], which initially was applied to A15 superconductors such as Nb₃Sn. Least squares fits to this model are shown as solid lines in both figures, revealing reasonable agreement for characteristic temperatures $T_0 = 123$ and 121 K, respectively. The differences of the residual resistivities may correspond to small differences in the filling of the 2(a)-sites by Ba or Sr. In case of the smaller atom Sr, filling seems to be more complete. The application of a magnetic field suppresses superconductivity of BaPt₄Ge₁₂ at fields above 2 T, while for SrPt₄Ge₁₂ the upper critical field $H_{c2}(0) \approx 1$ T (insets of Fig. 1).

The susceptibility χ exhibits a rather sharp transition at $T = 5.3$ and 5.1 K [inset, Fig. 2(b)], dropping from an initially small positive value to the diamagnetic value of $[-1/(4\pi)]$ for zero field cooling, which corresponds to a full Meissner Ochsensfeld effect. Magnetization measurements performed at various temperatures and magnetic fields up to 6 T evidence type II superconductivity. Upper critical field values are summarized in Fig. 3.

The heat capacity, C_p , of {Sr,Ba}Pt₄Ge₁₂ is plotted in Fig. 2 as C_p/T vs. T for zero and 3 T. For sake of clarity, measurements taken at intermediate field values are not shown here. The jump of $C_p(T)$ below 6 K evidences bulk superconductivity in both cases. An idealization of the heat capacity anomaly under the constraint of entropy balance between the superconducting and the normal state yields $T_c = 5.35$ and 5.1 K for

TABLE I: Normal state and superconducting properties of BaPt₄Ge₁₂ and SrPt₄Ge₁₂ which crystallize in the cubic skutterudite structure: space group Im $\bar{3}$, (No. 204); Ba and Sr are at the 2(a) (0, 0, 0) sites, Pt at the 8(c) ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) sites, and Ge at the 24g (0, y, z) sites. U_{eq} is a mean value of the atomic displacement ellipsoid.

property	BaPt ₄ Ge ₁₂	SrPt ₄ Ge ₁₂
lattice parameter a @300 K [nm]	0.86928(3)	0.86601(3)
Ge 24g site: y	0.15302	0.15197
Ge 24g site: z	0.35683	0.35536
$R_{F2} = \sum F_o^2 - F_c^2 / \sum F_o^2$	0.019	0.018
$U_{eq}(\{\text{Ba,Sr}\})$ [nm ²]	0.000066(2)	0.000118(3)
$U_{eq}(\text{Pt})$ [nm ²]	0.000062(1)	0.000069(1)
$U_{eq}(\text{Ge})$ [nm ²]	0.000092(2)	0.000097(2)
transition temperature T_c [K]	5.35	5.10
upper critical field $\mu_0 H_{c2}$ [T]	1.8	1
thermod. critical field $\mu_0 H_c$ [mT]	53	52
Fermi velocity v_F [m/s]	52500	67000
coherence length ξ [nm]	14(1)	18(1)
penetration depth λ [nm]	320(10)	250(10)
G.L. parameter κ	24(1)	14(1)

the Ba and Sr based compounds, respectively. Assuming that the specific heat of metallic compounds at low temperature follows $C_p = \gamma T + \beta T^3$, (γ is the Sommerfeld coefficient and β is proportional to the Debye temperature θ_D), least squares fits reveal $\gamma = 42$ mJ/molK² and $\theta_D = 247$ K (Ba) and $\gamma = 41$ mJ/molK² and $\theta_D = 220$ K (Sr). It is worth to be noted that the Debye temperature of BaPt₄Ge₁₂ is larger than that of SrPt₄Ge₁₂. In general, however, materials with smaller masses exhibit larger Debye temperatures. This anomaly observed may correspond to the fact that, while the volume of the unit cells of both compounds differ by only 1%, the atomic volumes of Sr and Ba differ by about 12 %. This causes a weaker bonding of Sr to the framework, hence a weaker force constant may result in lower values of θ_D .

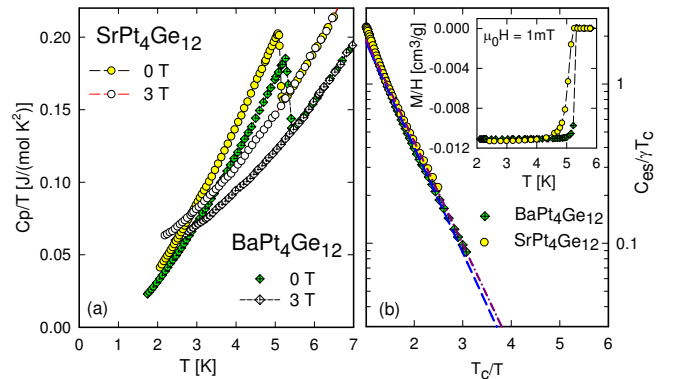


FIG. 2: (Color online) (a) Temperature dependent specific heat C_p of SrPt₄Ge₁₂ and BaPt₄Ge₁₂ plotted as C_p/T vs. T for 0 and 3 T. (b) Semi-logarithmic plot $C_{es}/\gamma T_c$ vs. T_c/T . The inset shows the low temperature and low field susceptibility M/H for both compounds.

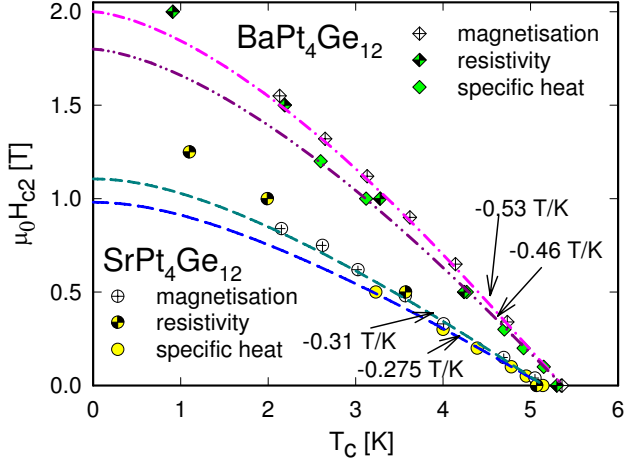


FIG. 3: (Color online) (a) Temperature dependent upper critical field $\mu_0 H_{c2}$ of $\text{BaPt}_4\text{Ge}_{12}$ and $\text{SrPt}_4\text{Ge}_{12}$ as obtained from resistivity, magnetization and specific heat measurements. The dashed and the dashed-dotted lines represent the WHH model.

Taking into account the McMillan model [12] allows calculation of the dimensionless electron-phonon coupling constant λ . Setting the repulsive screened Coulomb term $\mu^* \approx 0.13$, yields in both cases $\lambda \approx 0.7$. This refers to superconductors well beyond the weak coupling limit. In comparison, μ^* of different cage forming compounds covers a range from ≈ 0.1 to ≈ 0.3 [1, 2, 3].

The jump of the specific heat $\Delta C_p/T(T = T_c) \approx 58 \text{ mJ/molK}^2$ (Ba) and $\approx 57 \text{ mJ/molK}^2$ (Sr) allows calculation of $\Delta C_p/(\gamma_n T_c) \approx 1.35$, which is near to the figure expected from BCS theory [$\Delta C_p/(\gamma T_c) \approx 1.43$]. As the magnetic field strength increases (not shown here), both the transition temperature and the anomaly right at T_c are suppressed, constituting the phase diagram in Fig. 3.

The superconducting gap $\Delta(0)$ can be derived from a comparison of the modified BCS expression, $C_{es}(T) = 8.5\gamma T_c \exp(-0.82\Delta(0)/k_B T)$ with the experimental data depicted in a semi-logarithmic plot $C_{es}/\gamma T_c$ vs. T_c/T in Fig. 2(b) where $\text{BaPt}_4\text{Ge}_{12}$ and $\text{SrPt}_4\text{Ge}_{12}$ exhibit for $T_c/T > 2$ an exponential temperature dependence indicating a ratio $\Delta(0)/k_B T_c \approx 1.8$ in close agreement with the BCS value $\Delta_{\text{BCS}}(0) = 1.76 k_B T_c$.

The thermodynamic critical field is calculated from the free energy difference between the superconducting and normal state: $\Delta F(T) = F_n - F_s = \mu_0 H_c^2(T)/2$, where F_n and F_s are evaluated from the specific heat in the normal and superconducting state, respectively. The values obtained are $\mu_0 H_c(0) \approx 53(2)$ and $52(2)$ mT for Ba and the Sr-based compound, respectively.

Fig. 3 displays the temperature dependent upper critical field $\mu_0 H_{c2}$ of $\{\text{Sr}, \text{Ba}\}\text{Pt}_4\text{Ge}_{12}$ as deduced from field dependent resistivity, magnetization and heat capacity measurements. The slopes of the upper critical field $\partial(\mu_0 H_{c2})/\partial T \equiv \mu_0 H'_{c2}$ are collected in Table I, yielding slightly larger values deduced from magnetization and re-

sistivity data than those from specific heat, which may be attributed to pinning and surface effects. $\mu_0 H'_{c2}$ of $\text{BaPt}_4\text{Ge}_{12}$ is larger than $\mu_0 H'_{c2}$ of $\text{SrPt}_4\text{Ge}_{12}$.

Primarily, two mechanisms are responsible for the limited value of $\mu_0 H_{c2}$: orbital pair breaking and Pauli limiting. Werthamer et al. [13] derived an expression (*WHH model*) for the upper critical field $\mu_0 H_{c2}$ in terms of orbital pair-breaking, including the effect of Pauli spin paramagnetism and spin-orbit scattering. A comparison of the experimental results with the WHH model is based on two parameters, α , the Pauli paramagnetic limitation (*Maki parameter*) and λ_{so} describing spin-orbit scattering. If the atomic numbers of the elements constituting the material increase, λ_{so} is expected to increase as well.

The Maki parameter α can be estimated via the Sommerfeld value γ and ρ_0 [13], i.e., $\alpha = (3e^2 \hbar \gamma \rho_0)/(2m\pi^2 k_B^2)$ with e the electron charge and m the electron mass. Taking the experimental ρ_0 and γ yields $\alpha = 0.18$ for $\text{BaPt}_4\text{Ge}_{12}$ and $\alpha = 0.14$ for $\text{SrPt}_4\text{Ge}_{12}$. We have adjusted the WHH model to the experimental data (dashed and dashed-dotted lines in Fig. 3), revealing $\lambda_{so} \approx 15$ for all data-sets.

The thermodynamic and the upper critical field are used to calculate the ratio of the penetration depth $\lambda_{\text{GL}}(0)$ to the coherence length $\xi_{\text{GL}}(0)$ via Abrikosov's relation $\lambda_{\text{GL}}(0)/\xi_{\text{GL}}(0) \equiv \kappa_{\text{GL}}(0) = H_{c2}/[\sqrt{2}H_c(0)]$ yielding the Ginzburg-Landau parameter $\kappa_{\text{GL}} = 24(2)$ and $14(2)$ for the Ba and Sr-based compounds. The absolute values of the coherence length ξ_0 and the penetration depth $\lambda(0)$ can be evaluated via the isotropic Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory. Values obtained are presented in Table I.

The Fermi velocity v_F can be calculated from the Fermi surface area S_s as shown by Orlando et al. [14]. Values are given in Table I. Combining S_s and ρ_0 , a mean free path l_{tr} of about $\approx 1.0 \cdot 10^{-8}$ m and $\approx 1.4 \cdot 10^{-8}$ m for the Ba and Sr compound, respectively, is derived.

The fact that $\mu_0 H'_{c2}$ of $\text{BaPt}_4\text{Ge}_{12}$ is larger than that of $\text{SrPt}_4\text{Ge}_{12}$ can be understood in terms of the Ginzburg-Landau theory. Hake [15] and Orlando et al. [14] derived a model equation for $\mu_0 H'_{c2}$ which primarily depends on two parameters: on the inverse of the square of v_F and on the inverse of l_{tr} . Taking into account the parameters deduced from the above analyses explains in both cases, at least qualitatively, differences of $\mu_0 H'_{c2}$. While the decrease of v_F from the Sr to the Ba case can be conceived by an increase of the unit cell volume ($v_F \propto (N/V)^{1/3}$, for free electrons), the decrease of the mean free path corresponds to the increase of the residual resistivity from $\text{SrPt}_4\text{Ge}_{12}$ to $\text{BaPt}_4\text{Ge}_{12}$.

From $l_{tr}/\xi \approx 1$ we classify $\{\text{Ba}, \text{Sr}\}\text{Pt}_4\text{Ge}_{12}$ as a dirty limit superconductor, and κ of the order of 10 to 20 refers to a pronounced type II superconducting behavior.

The DOS in Fig. 4 reveal the individual contributions of X=(Ba,Sr), Pt and Ge atoms showing that Ge states, which are of *p*-like character, are dominating at Fermi energy. The Ge states hybridize with Pt 5*d*-like states by which the spin-orbit coupling effect is transmitted to the

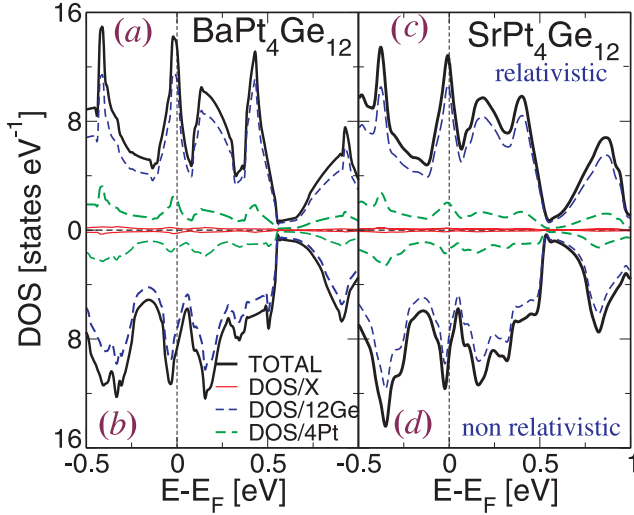


FIG. 4: (Color online) DOS for $\text{BaPt}_4\text{Ge}_{12}$ (a,b) and $\text{SrPt}_4\text{Ge}_{12}$ (c,d) as derived from DFT calculations. Fermi energy is situated at zero energy. The upper half (a),(c) shows the density of states for a fully relativistic calculation, which includes spin-orbit (SO) coupling. The lower half (b),(d) of the figure presents the DOS of a standard non-relativistic calculation. The total DOS is decomposed into the local DOS representative for one Ba(Sr), four Pt, and twelve Ge atoms. The relativistic effect is small but important, because it shifts the Fermi level of the non-relativistic DOS almost into the maximum of the relativistic DOS.

DOS at E_F . Consequently, by making use of the electron localization function technique [?], expressive Ge-Ge covalent bonds and typical metallic Pt bonding are being deduced. The metallic features of the DOS around E_F convincingly confirm that the Zintl concept no longer applies to $\{\text{Sr}, \text{Ba}\}\text{Pt}_4\text{Ge}_{12}$, while its applicability is quite obvious among pnictogen-based skutterudites.

The total DOS at E_F can be compared with the Som-

merfeld value of the specific heat $\gamma = \frac{1}{3}\pi^2 N(E_F)k_B^2$. The experimental values slightly larger than 40 mJ/molK^2 for the Ba and Sr compounds, along with an electron-phonon enhancement factor $\lambda_{ep} = 0.7$ (estimated via the McMillan formula [12]) would require a bare DOS equivalent to $\approx 25 \text{ mJ/molK}^2$, which compares favorably with the DOS calculations involving spin-orbit coupling: 31 mJ/molK^2 for the Ba ($N(E_F) = 13.2 \text{ states eV}^{-1} \text{ f.u}^{-1}$) and 28 mJ/molK^2 for the Sr compound ($N(E_F) = 12.1 \text{ states eV}^{-1} \text{ f.u}^{-1}$). Without spin-orbit coupling, the specific heats, γ , are 19.5 and 21.0 mJ/molK^2 for Ba and Sr, respectively. This implies the importance of the relativistic effects.

In summary, superconducting $\{\text{Sr}, \text{Ba}\}\text{Pt}_4\text{Ge}_{12}$ are the first skutterudites where the framework in the structure is entirely built by Ge-atoms. DFT calculations proved that $X = (\text{Ba}, \text{Sr})$ guest atoms strongly stabilize the compounds. Most strikingly, the calculated DOS around E_F is composed of hybridized Ge $4p$ -like and Pt $5d$ -like states, and it has a sharp peak with its maximum very close to E_F . The influence of the guest atoms (Ba or Sr) on superconductivity, however, may be ruled out due to the fact that (i) the Ba- or Sr-like DOS around E_F is negligible and (ii) the DOS around E_F for the *hypothetical* X-free $\text{Pt}_4\text{Ge}_{12}$ framework is very similar to the one of $X\text{Pt}_4\text{Ge}_{12}$ ($X = \text{Ba}$ and Sr). Hence, superconductivity appears to be an intrinsic property of the Pt-Ge cage-forming structure. This conclusion is in line with the slightly smaller value of T_c observed in $\text{SrPt}_4\text{Ge}_{12}$, in marked contrast to the isotope effect, where lighter masses would originate larger SC transition temperatures.

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